

Ozone as an Analytical Reagent

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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Lynne Lionel Merritt, Jr.
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Ozone as an Analytical Reagent

Determination of Vanadium, Cerium, and Manganese

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OZONE is an exceedingly powerful oxidizing agent. The normal oxidation potential as given by Kassel (3) for the reaction



is 2.07 volts. Only fluorine and atomic oxygen have higher oxidation potentials. Ozone is much easier to produce and to handle than either fluorine or atomic oxygen, and, therefore, should be useful where a very powerful oxidizing agent is required. Furthermore, ozone is a gas and its decomposition and reduction product, oxygen, is also a gas, and both may easily be removed merely by warming or by passing some inert gas through the solution. Thus oxidations may be produced without adding any foreign matter.

The action of ozone on inorganic compounds has been previously investigated by a great number of workers. In practically all cases prolonged action results in the formation of a compound of the highest stage of oxidation of the element under consideration. Most investigators did not determine whether a given compound could be quantitatively changed to a definite oxidized state.

Jannasch and Gottschalk (2) devised a method for the determination of manganese by oxidizing manganous salts to manganese dioxide by means of a current of ozone. Noyes and Garner (4) used ozone to prepare thallic nitrate from thallous nitrate and found that the oxidation was quantitative.

Experimental

APPARATUS. The ozonizer employed in this investigation (Figure 1) was essentially that described by Noyes, Hoard, and Pitzer (5). It was constructed from two coaxial Pyrex cylinders, *F* and *G*, with an air space of about 3 mm. between them. The diameter of the inner cylinder was about 25 mm. and the length 45 cm. The outer tube was sealed to the inner tube at the top and the inner tube was sealed off at its lower end. The lower end of the outer tube was drawn down and sealed to a smaller tube

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bent at right angles and carrying the male half of a standard-taper glass joint, *J*. Oxygen entered through a side arm, *B*, at the top of the apparatus and left through the standard-taper glass joint. A coil of aluminum sheet, *H*, placed inside the inner tube served as one electrode and a similar coil, *E*, wound around the outer glass tube served as the second electrode. The outer electrode was surrounded by a glass cylinder, *D*, through which tap water was circulated to cool the whole apparatus. Water entered at *I* and left at *K*. Rubber stoppers, *C*, were used to hold the cooling jacket in place. A 15,000-volt, 850-watt, 60-cycle transformer supplied current to the two electrodes through connections *A* and *L*.

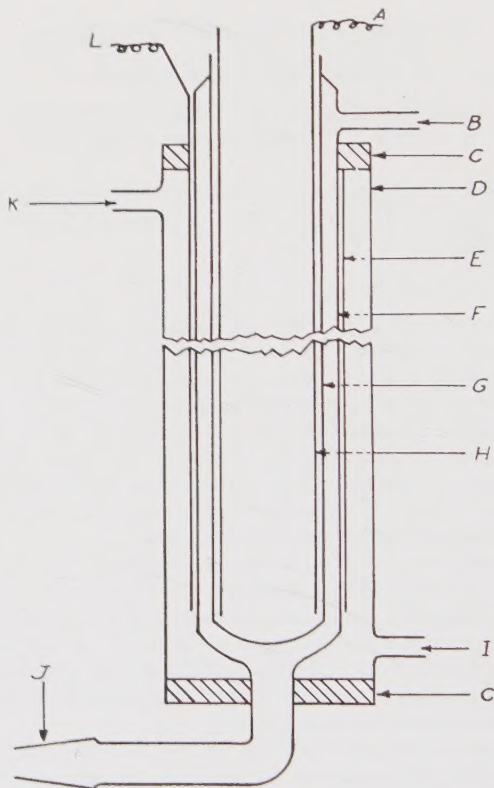


FIGURE 1. OZONIZER

The ozone was led into the solutions by means of a bubbler tube which was constructed by cutting off the top of a Jena fritted-glass funnel approximately 32 mm. in diameter. The edges were ground down until there was no projection of glass above the fritted-glass disk. The stem of the funnel was sealed to a Pyrex tube bent at right angles and terminated by the female half of a standard-taper glass joint. The bubbler tube reached nearly to the bottom of a large 25-cm. (10-inch) test tube. Rapid oxidation depends largely upon getting intimate contact between the gas and solution—that is, the gas bubbles should be as small as possible.

Oxygen was supplied from a tank and was dried by passage over anhydrous magnesium perchlorate. The ozonizer was placed in a hood, since ozone is very irritating to the mucous

membranes of the body. Rubber tubes carrying oxygen and water were partially protected from the deteriorating action of ozone by dipping the tubes in molten beeswax.

A T-tube was placed in the oxygen inlet line, so that carbon dioxide or nitrogen could be substituted for oxygen in order to sweep out oxygen and ozone from the solutions.

The gas issuing from the ozonizer at the rate of about 10 liters per hour contained approximately 5 per cent ozone by weight if the outer electrode was not grounded and about 2 per cent by weight when the outer electrode was grounded.

PREPARATION OF REAGENTS. Potassium permanganate solution was prepared in the usual way and standardized against Bureau of Standards sodium oxalate by the procedure of Fowler and Bright (1). This was reduced with hydrogen peroxide in dilute perchloric acid solution and diluted to a known volume to give a standard solution of manganous perchlorate.

Standard solutions of ferrous sulfate were kept under carbon dioxide. The ferrous sulfate was standardized regularly against standard potassium permanganate solutions.

A solution of cerous nitrate was prepared from pure cerous nitrate crystals. This solution was standardized by oxidation with persulfate, using silver ion as catalyst, and subsequent titration of the ceric ion with standard ferrous sulfate according to the method of Willard and Young (7). The ferrous sulfate was standardized against potassium dichromate.

The silver nitrate solution used as a catalyst contained 35 grams of silver nitrate per liter.

Determination of Manganese

In perchloric acid solutions containing a little silver ion as catalyst, manganous ion is rapidly oxidized to permanganate ion. In nitric acid, phosphoric acid, or sulfuric acid solutions oxidation is incomplete or manganese dioxide is precipitated.

GENERAL PROCEDURE. A measured quantity of the standard manganous perchlorate solution was added to the desired quantity of perchloric acid and diluted to 100 ml. in a 25-cm. (10-inch) test tube. Silver nitrate solution was added and the solution so prepared was subjected to a stream of ozone from the ozonizer. The gas flow was always about 10 liters per hour. After the desired period of oxidation, carbon dioxide was substituted for oxygen and the excess oxygen and ozone were thus swept out of the solution; this required 15 minutes.

The bubbler tube was rinsed into the solution with distilled water and a measured excess of standard ferrous sulfate was added. The excess ferrous sulfate was back-titrated with standard potassium permanganate. The small amount of potassium permanganate necessary to give the pink color at the end point was determined each time by adding standard permanganate

TABLE I. INFLUENCE OF PERCHLORIC ACID CONCENTRATION

Perchloric Acid Molarity	Mn Present Mg.	Mn Found Mg.	Error Mg.
1.16	3.22	3.16	-0.06 ^a
1.39	3.22	3.24	+0.02
1.39	3.22	3.19	-0.03
1.74	3.22	3.29	+0.07
1.74	3.22	3.26	+0.04
2.32	3.22	3.23	+0.01
3.48	3.22	3.26	+0.04
3.48	3.22	3.01	-0.21
4.64	3.22	3.11	-0.11
5.80	3.22	1.87	-1.35
5.80	3.22	2.55	-0.67

^a A slight precipitate of MnO_2 was noted on bubbler tube.

solution to an equal volume of acid until the same shade of pink was obtained. This usually amounted to 0.03 to 0.05 ml. of 0.1 *N* permanganate and was subtracted from the amount used in the back-titration.

INFLUENCE OF PERCHLORIC ACID CONCENTRATION. Solutions containing 3.22 mg. of manganese and 35 mg. of silver nitrate were treated as described above (Table I). Ozone was passed through the solutions for one hour. The concentration of perchloric acid present was varied from 1.16 *M* to 5.80 *M*. With a concentration of perchloric acid less than 1.16 *M* a precipitate of manganese dioxide always appeared. The results became erratic at concentrations of acid higher than 2.32 *M*.

INFLUENCE OF SILVER NITRATE CONCENTRATION ON TIME NECESSARY FOR COMPLETE OXIDATION. With no silver nitrate present in the solutions about 6 hours were required for complete oxidation; with 17.5 mg. of silver nitrate per 100 ml., 2 hours; with 35 mg., 1 hour; and with 70 mg. 0.5 hour. In these trials an ozone concentration of about 2 per cent by weight was used, rather than 5 per cent, since the effect of silver nitrate is more pronounced with the lower ozone concentrations. In subsequent experiments a concentration of 35 mg. of silver nitrate per 100 ml. of solution was employed.

INFLUENCE OF OZONE CONCENTRATION ON SPEED OF OXIDATION AND ON AMOUNT OF MANGANESE OXIDIZED. If a gas stream having an ozone concentration of 2 per cent by weight was employed, only 5 mg. of manganese could be oxidized without precipitation of manganese dioxide. The time necessary for complete oxidation was from 60 to 75 minutes. With an ozone concentration of 5 per cent, about 9 mg. of manganese could be oxidized in 15 minutes without precipitation of manganese dioxide.

INTERFERENCES. All substances which are oxidized by ozone and subsequently reduced by ferrous sulfate but not reoxidized by potassium permanganate will interfere; this includes cerium, cobalt, and chromium. Vanadium interferes unless care is taken that the pink color is permanent in the back-titration with permanganate.

Chlorides and all other ions which precipitate silver must be absent. Large concentrations of nitrates will interfere, since they oxidize ferrous salts.

Recommended Procedure for Determining Manganese in Steel and Iron Ore

STEEL. Dissolve 1 gram of the steel, or a sample which will contain not more than 9 mg. of manganese in about 5 ml. of nitric acid diluted with 15 to 25 ml. of water. After all the steel has dissolved, add 25 ml. of 70 to 72 per cent perchloric acid and evaporate until fumes of perchloric acid appear, to remove nitric acid. Allow the beaker and contents to cool and then add 1 ml. of a silver nitrate solution containing 35 grams of silver nitrate per liter. Transfer the solution to a 25-cm. (10-inch) test tube and dilute to approximately 100 ml. with water. Bubble 5 per cent ozone through this solution for 15 minutes.

After 15 minutes of oxidation, pass carbon dioxide through the solution for 15 minutes, remove the bubbling tube from the

ozonizer, and rinse it several times with distilled water. Add an accurately measured excess of standard ferrous sulfate (20.00 ml. of 0.05 *N* ferrous sulfate is sufficient) and back-titrate immediately with standard potassium permanganate until a faint pink color persists. Determine the excess permanganate necessary to give this pink color by adding permanganate to the same volume of water or dilute acid until the colors in blank and experiment match. Usually 0.03 to 0.05 ml. of 0.10 *N* potassium permanganate is required. Subtract the blank from the volume of standard permanganate used in the experiment.

IRON ORE. Dissolve 1 gram of the ore, or a weight which contains not more than 9 mg. of manganese, in 40 ml. of hydrochloric acid (3 to 1). After all iron oxide has gone into solution and only flocculent white silica remains, add 25 ml. of concentrated nitric acid and 25 ml. of 70 to 72 per cent perchloric acid, and evaporate the solution to fumes of perchloric acid. After the solution has cooled, transfer it to a 25-cm. (10-inch) test tube, add 2 ml. of silver nitrate solution (35 grams of silver nitrate per liter), and dilute to about 100 ml. Pass ozone through the solution for 15 minutes and proceed exactly as described above for a steel.

RESULTS OF ANALYSES. Results of analyses on National Bureau of Standards samples of iron ores and steels according to the procedures described above are given in Table II.

TABLE II. DETERMINATION OF MANGANESE IN STEEL AND IRON ORE

Sample	Weight of Sample Gram	Mn Found %	Certificate Value %
Bur. of Standards iron ore No. 28	0.9380	0.449	0.465
	0.8992	0.439	
Bur. of Standards steel No. 96	1.0040	0.733	0.747
	1.0713	0.739	
Bur. of Standards steel No. 11c	1.0278	0.429	0.435
	1.2600	0.436	
	1.2469	0.426	
	1.7630	0.433	

Determination of Cerium

Preliminary experiments showed that ozone did not oxidize cerous salts in perchloric acid solution and only partially in sulfuric acid solution, but it quantitatively oxidized them to ceric salts in solutions containing both sulfuric and phosphoric acids, although the oxidation with gas containing 2 per cent ozone was very slow. Ceric phosphate, being much more insoluble than cerous phosphate, separates out of the solution in the form of a thick white gel. Unless the cerium is precipitated in this way, oxidation is incomplete.

PROCEDURE. Take for analysis a sample containing not more than 100 mg. of cerium, and to this solution add 2 ml. of concentrated sulfuric acid and 5 ml. of sirupy phosphoric acid (80 per cent). Dilute the solution to 100 ml. and treat with 5 per cent ozone for 60 minutes. Add concentrated sulfuric acid until the white gel of ceric phosphate dissolves completely and a clear yellow-orange solution results. About 15 to 20 ml. of acid is required. Pass carbon dioxide or nitrogen through the solution for 15 minutes to remove oxygen and ozone. Remove the bubbling tube from the solution and carefully rinse with distilled water. Add 2 drops of *o*-phenanthroline ferrous sulfate solution

(0.025 *M*) and titrate the ceric sulfate with standard ferrous sulfate until the indicator changes to a bright pink.

In the presence of large amounts of iron, 7 ml. of phosphoric acid, rather than 5 ml. as specified, are added to the solution.

RESULTS OF ANALYSES. Results of several analyses by the method described above are listed in Table III. Amounts of cerium greater than about 100 mg. are not readily handled,

TABLE III. DETERMINATION OF CERIUM

Cerium Taken <i>Mg.</i>	Other Additions	Cerium Found <i>Mg.</i>	Error <i>Mg.</i>
100.00		99.83	-0.17
77.37		77.40	+0.03
72.03		71.87	-0.16
57.64		57.61	-0.03
57.62		57.94	+0.32
43.22		43.16	-0.06
43.22		43.13	-0.09
28.81		28.78	-0.03
14.41		14.21	-0.20
93.64	2 mg. Cr ⁺⁺⁺	93.43	-0.21
86.44	1 gram Fe ⁺⁺⁺	86.09	-0.35
86.44	1 gram Fe ⁺⁺⁺	86.21	-0.23
72.03	2 mg. Cr ⁺⁺⁺	72.00	-0.03
72.03	1 gram Fe ⁺⁺⁺	71.94	-0.09
28.81	1 gram Fe ⁺⁺⁺ and 2 mg. Cr ⁺⁺⁺	28.95	+0.14

owing to the large amount of gelatinous ceric phosphate which is formed, and the oxidation takes longer than one hour.

INTERFERENCES. It is apparent from Table III that iron and small amounts of chromium do not interfere. All substances which are oxidized by ozone in acid solution and are reduced by ferrous sulfate must be absent. This includes manganese, cobalt, vanadium, and large amounts of chromium salts. Chlorides and large concentrations of nitrates should not be present.

Determination of Vanadium

In preliminary experiments it was found possible to oxidize vanadyl salt solutions completely to vanadates by means of ozone. The oxidation of chromium was very slow in the cold and in the absence of a catalyst. These two observations suggested that ozone could be substituted for potassium permanganate in the Willard and Young (6) method for the determination of vanadium in chromium-vanadium and chromium-vanadium-tungsten steels. Such was found to be the case.

The completion of the oxidation of the vanadyl ion may be easily judged by adding a small amount of manganous salt to the solution before oxidation. When all vanadyl ion is oxidized, the ozone will begin to oxidize manganese to permanganate. The appearance of a permanganate color thus serves as an indication of the complete oxidation of all vanadium. Many steels contain sufficient manganese without further addition.

PROCEDURE FOR CHROMIUM-VANADIUM STEELS. Weigh out a sample of approximately 5 grams of the chromium-vana-

dium steel and dissolve in approximately 30 ml. of water and 3 ml. of concentrated sulfuric acid with 1.5 ml. additional acid for each gram of steel. After all action has ceased evaporate the solution until considerable salts begin to separate, in order to decompose carbides. Add approximately 50 ml. of water, and then add to the boiling hot solution concentrated nitric acid drop by drop until the vigorous oxidation of ferrous salts is completed. After boiling for 2 to 3 minutes to remove oxides of nitrogen, cool the solution to room temperature, add 25 ml. of 1 to 1 phosphoric acid, dilute the solution to 300 ml., and connect to the ozonizer. The concentration of ozone in the gas should be about 5 per cent by weight. (With this concentration the oxidation of vanadyl salts is complete in about 5 minutes.) As soon as a definite permanganate color appears remove the solution from the ozonizer and carefully rinse the bubbling tube into the sample. Remove the permanganate by reduction with azide or nitrite and titrate the solution with ferrous sulfate, using oxidized diphenylamine as indicator as described by Willard and Young (6), or potentiometrically.

If tungsten is present, it is kept in solution as complex fluoride and the procedure of Willard and Young (6) is followed.

TABLE IV. DETERMINATION OF VANADIUM IN STEELS

Sample	Vanadium		Error %
	Present %	Found %	
Bur. of Standards Cr-V steel No. 30c	0.235	0.231	-0.004
		0.237	+0.002
		0.234	-0.001
		0.236	+0.001
Bur. of Standards Cr-V steel No. 30a	0.20	0.199	0.00
		0.204	0.00
		0.199 ^a	0.00
Steel sample No. 6	0.218 ^b	0.215	-0.003
		0.217	-0.001
Steel sample No. 19	0.230 ^b	0.228	-0.002
		0.228	-0.002
Steel sample No. 20	0.139 ^b	0.143	+0.004
		0.144	+0.005
Bur. of Standards, Cr-V-W steel No. 50a	0.976	0.998	+0.022
		0.994	+0.018
		0.990	+0.014
		0.984	+0.008
Bur. of Standards Cr-V-W steel No. 50	0.756	0.783	+0.027
		0.765	+0.009
		0.762	+0.006
		0.746	-0.010

^a End point determined potentiometrically.

^b Value determined by permanganate method of Willard and Young (6).

RESULTS OF ANALYSES. Results of a series of determinations according to the method described above (Table IV) are slightly higher than those recommended by the Bureau of Standards for the chromium-vanadium-tungsten steels.

Action of Ozone on Compounds of Other Elements

Chromic ion in acid solution was scarcely oxidized unless silver nitrate was present as catalyst and even then only in small amounts.

Iodide in alkaline solution was oxidized to periodate and this reaction will be described in a subsequent paper. Bro-

midic under similar conditions was partially oxidized to bromate. Chloride ion was not affected.

Selenite and tellurite ions were quantitatively oxidized to selenate and tellurate in alkaline solution, but there was only slight oxidation in acid solution.

Trivalent arsenic and antimony were completely oxidized in acid or alkaline solution.

Mercurous perchlorate was readily oxidized to the mercuric form.

Lead in alkaline solution was partially oxidized and bismuth formed a brown precipitate of a higher oxide, probably Bi_2O_4 .

Cobaltous and nickelous hydroxides formed the corresponding trivalent hydroxides.

Nitrite was oxidized to nitrate; hypophosphite and phosphite were oxidized to phosphate.

Summary

Manganese can be quantitatively oxidized to permanganate by ozone if the amount of manganese does not exceed 9 mg. and the oxidation is carried out in a perchloric acid solution between 1.16 and 2.32 *M*, using silver nitrate as catalyst. Oxidation requires about 15 minutes if oxygen containing 5 per cent ozone by weight is used. Procedures are given for the determination of manganese in steel and iron ore.

Up to 100 mg. of cerium can be oxidized in 1 hour to ceric phosphate by ozone in a solution containing sulfuric and phosphoric acids. Ceric phosphate separates in the form of a white gel which is dissolved by sulfuric acid and the ceric ion is titrated with ferrous sulfate.

Vanadium in chromium-vanadium and chromium-vanadium-tungsten steels may be determined after oxidation by ozone to vanadic acid.

Iodides, selenites, tellurites, nitrites, hypophosphites, and phosphites are oxidized by ozone. Mercurous, arsenious, and antimonous ions are also oxidized. Chromic and bromide ions are only partially oxidized.

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From a thesis presented by Lynne L. Merritt, Jr., to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of doctor of philosophy.

Determination of Iodides

OZONE can be used in the determination of manganese, vanadium, and cerium (3). It will also quantitatively oxidize iodide ion to periodate ion in solutions alkaline with sodium or potassium hydroxide. In sodium carbonate solutions iodide is oxidized mainly to iodate, but there is some further oxidation to periodate. Some iodine is lost as iodine pentoxide which is carried out of the solution in the form of white fumes by the bubbles of oxygen and ozone. Quantitative oxidation of iodide to iodate could not be secured, even though buffered solutions of varying pH values and sodium and potassium carbonate solutions of varying concentrations were tried.

Periodates may be determined by either of two methods. In a buffered neutral solution periodate reacts with iodide ion to form iodine and iodate according to the equation:



Willard and Boyle (2) have found that a buffer consisting of 5 grams of boric acid and 5 grams of borax per 100 ml. of solution is satisfactory for this reaction. The liberated iodine is titrated with standard, neutral, arsenite solution. Periodates may also be determined by allowing them to react with excess iodide in the presence of excess acid:



The liberated iodine is titrated with standard sodium thiosulfate.

The first method of determining the periodate formed by the oxidation of iodide by ozone should be especially useful for large amounts of iodine, since only two atoms of iodine are formed for the final titration from each iodide ion present at the start. The second method of titration is especially useful for the determination of small amounts of iodide ion, since eight atoms of iodine are present for the final titration for each iodide ion in the original solution.

Experimental

PREPARATION OF SOLUTIONS. **Standard Iodide Solution.** An approximately 0.1 *M* solution of potassium iodide (Mallinckrodt's analytical reagent grade) was carefully standardized against a solution of potassium permanganate which, in turn, was standardized against Bureau of Standards arsenious oxide. The procedure was that described by Kolthoff, Laitinen, and Lingane (1). Weight burets were used and all end points were determined potentiometrically. The solution was found to contain 0.015688 gram of iodine per gram of solution (weighed in air against brass weights).

Sodium Thiosulfate Solution. An approximately 0.1 *N* sodium thiosulfate solution was carefully standardized every few days against iodine which had been sublimed once from potassium iodide and then twice resublimed and dried over calcium

chloride. Portions of this purified iodine were fused in a tared weighing bottle, cooled, and weighed, and the bottle was opened under a 20 per cent solution of potassium iodide. The iodine was titrated with the sodium thiosulfate solution using starch as indicator. This procedure was also checked by standardizing the thiosulfate against the potassium permanganate used to standardize the iodine solution described above. The results agreed within 3 parts in 10,000 with the standardizations against purified iodine. Weight burets were used in all titrations.

Another solution of thiosulfate was prepared in a similar manner, but ordinary volume burets were used for the titrations.

Standard Arsenite Solution. Bureau of Standards arsenious oxide (6.5200 grams) was dissolved in 100 ml. of water containing 15 grams of sodium hydroxide crystals (monohydrate). This solution was diluted to about 1.5 liters, saturated with carbon dioxide, and then diluted to exactly 2 liters in a volumetric flask. One milliliter thus corresponds to 0.004183 gram of iodine originally present, since two atomic weights of iodine are formed by each mole of periodate.

PROCEDURE. A weighed portion of the standard iodide solution was added to the desired amount of sodium or potassium hydroxide containing any other desired additions. This solution was diluted to approximately 100 ml. in a 25-cm. (10-inch) test tube and connected to the ozonizer described in the previous paper (3). The gas containing about 5 per cent by weight of ozone was passed into the solution at such a rate that the bubbles from the bubbling tube rose to form a fine layer of foam on top of the solution (about 10 liters of gas per hour). After the desired time of oxidation, the current was turned off and the oxygen was stopped. Nitrogen was passed through the solution for 15 minutes to remove all dissolved ozone and oxygen. The solution was rinsed into a flask and titrated by one of the two following methods.

1. *Reduction of Periodate to Iodate.* Eight grams of boric acid were added to the solution for every gram of sodium hydroxide (or 1.5 grams of sodium hydroxide crystals) present in the original solution. The solution was stirred and warmed slightly, if necessary, to dissolve the boric acid. This amount of acid is enough to convert the sodium hydroxide to borax and to give an equal weight of excess boric acid. Ten to 20 grams of potassium iodide were added and the liberated iodine was titrated with standard arsenite solution using starch as indicator.

2. *Reduction of Periodate to Iodine.* Ten grams of potassium iodide were added to the solution, which was then acidified with 6 *N* sulfuric acid, using 5.5 ml. of acid for every gram of sodium hydroxide (or 1.5 grams of sodium hydroxide crystals) originally present. The liberated iodine was titrated with standard thiosulfate solution, using starch as indicator.

TABLE I. PERMISSIBLE LIMITS OF ALKALI CONCENTRATION

Alkali Concentration	Time of Oxidation Min.	Iodide Taken Gram	Iodide Found Gram	Error Gram
2% Na ₂ CO ₃	90	0.1704	0.1261	-0.0443
4% Na ₂ PO ₄	90	0.1553	0.1298	-0.0255
1% NaOH	30	0.0695	0.0695	-0.0000
2% NaOH	40	0.1498	0.1497	-0.0001
10% NaOH	30	0.0640	0.0639	-0.0001

PERMISSIBLE LIMITS OF ALKALI CONCENTRATION. Several analyses were made by the second procedure, using known quantities of iodide ion and varying the concentration of alkali present (Table I). It is obvious that any concentration of sodium hydroxide from 1 per cent to at least 10 per

cent may be present during the oxidation. Sodium carbonate or tribasic sodium phosphate solutions are not alkaline enough for complete oxidation. Oxidation in these solutions has been shown to stop with the iodine largely present as iodate.

TABLE II. AMOUNT OF IODINE OXIDIZED

Time of Oxidation <i>Min.</i>	Iodide Taken <i>Gram</i>	Iodide Found <i>Gram</i>	Error <i>Gram</i>
15	0.0541	0.0272	-0.0269
15	0.1680	0.0954	-0.0736
20	0.1651	0.1653	+0.0002
30	0.1866	0.1864	-0.0002
30	0.1992	0.1992	±0.0000

AMOUNT OF IODIDE OXIDIZED IN A GIVEN TIME. Analyses were carried out by the procedure described above, using 2 per cent sodium hydroxide solutions for the oxidation (Table II). All titrations of periodate were made according to method 1, using neutral arsenite solution.

It is apparent that 20 minutes is the minimum time for the complete oxidation, using a gas containing about 5 per cent ozone by weight. Thirty minutes is recommended. With 2 per cent ozone the time is greatly extended. In one experiment only 4.4 per cent of the theoretical amount of periodate had been formed after 80-minute oxidation of a solution containing 0.17908 gram of iodine.

About 0.2 gram of iodine as iodide is the upper limit for convenient handling. More than this amount requires more than 50 ml. of 0.1 *N* arsenite solution and some of the iodine liberated is liable to volatilize from the solution and be lost. About 0.05 gram of iodine is the upper limit for convenient handling when the periodate is titrated with thiosulfate by method 2.

INTERFERENCES. Tests were carried out by the procedures described above on solutions containing known amounts of iodide ion with various other additions (Table III). It is

TABLE III. EFFECT OF CHLORIDES AND BROMIDES

Addition	Method of Titration	Iodide Taken <i>Gram</i>	Iodide Found <i>Gram</i>	Error <i>Gram</i>
2 grams NaCl	Arsenite	None	0.00000	0.00000
3 grams NaCl	Arsenite	0.08554	0.08581	0.00027
	Arsenite	0.15533	0.1550	-0.0003
	Arsenite	0.16800	0.16853	0.00053
	Thiosulfate	0.01104	0.01102	-0.00002
	Thiosulfate	0.01157	0.01151	-0.00006
3 grams KCl ^a	Arsenite	None	0.0000	0.0000
3 grams KCl ^a	Arsenite	0.16731	0.1678	0.0005
3 grams KCl	Arsenite	0.04760	0.04745	-0.00015
	Thiosulfate	0.01264	0.01258	-0.00006
0.6 gram KBr, 2 grams NaCl	Arsenite	None	0.00807	0.00807
2 grams KBr, 2 grams NaCl	Arsenite	None	0.00636	0.00636
2 grams KBr, 2 grams NaCl ^b	Arsenite	None	0.00900	0.00900

^a Potassium hydroxide substituted for sodium hydroxide.

^b Solution kept near boiling during oxidation.

apparent that bromide ion interferes with either method of titration of the periodate but that chlorides do not interfere. Potassium hydroxide may be substituted for sodium hydroxide. If other iodine compounds are present they will also be oxidized to periodate.

Recommended Procedure

To a portion of the solution containing not more than 0.2 gram of iodine as iodide or iodate 2 grams of sodium hydroxide (or 3 grams of sodium hydroxide crystals, $\text{NaOH} \cdot \text{H}_2\text{O}$) were added. The clear solution was diluted to 100 ml. in a 25-cm. (10-inch) test tube and ozone was passed through it for 30 minutes. The gas should contain about 5 per cent ozone by weight and a speed of about 10 liters of gas per hour is sufficient. Nitrogen was substituted for oxygen and the solution was swept free of dissolved ozone and oxygen for 15 minutes. The bubbler tube was removed and both bubbler tube and solution were rinsed into a large wide-mouthed flask.

Two procedures may be followed from this point. Procedure A is recommended for small amounts of iodine (up to about 0.05 gram) and B for large amounts (0.05 to 0.2 gram).

PROCEDURE A. TITRATION WITH THIOSULFATE. To the solution in a large flask 10 grams of iodate-free potassium iodide were added and then 11 ml. of 6 *N* sulfuric acid (5.5 ml. for each gram of sodium hydroxide). The liberated iodine was titrated with standard sodium thiosulfate solution. When the solution was still faintly yellow 1 ml. of 2 per cent starch solution was added as indicator, and it was titrated to a clear, colorless solution. In determining small amounts of iodine a blank should be run.

PROCEDURE B. TITRATION WITH ARSENITE. Sixteen grams of boric acid (8 grams for each gram of sodium hydroxide) were added to the solution contained in a wide-mouthed flask, warming slightly if necessary to dissolve the boric acid. The solution was cooled to room temperature and 10 grams of potassium iodide were added. The liberated iodine was titrated with standard arsenite solution, and when the solution became faintly yellow, 1 ml. of 2 per cent starch indicator solution was added and the titration continued until the dark starch-iodine color disappeared.

Results of Analyses

Results of a series of analyses by the procedures described above are listed in Table IV.

TABLE IV. DETERMINATION OF IODIDE BY OZONE

Iodide Present Gram	Other Additions	Titration Method	Iodide Found Gram	Error in Iodide Gram
0.16356	...	A ^a	0.16352	-0.00004
0.10563	...	A ^a	0.10533	-0.00030
0.06720	...	A	0.06731	+0.00011
0.01408	...	A	0.01408	±0.00000
0.00729	...	A	0.00725	-0.00004
0.00462	...	A	0.00461	-0.00001
0.00051	...	A ^b	0.00051	±0.00000
0.00051	...	A ^{b, c}	0.00043	-0.00008
0.04970	3 grams NaCl	A	0.04945	-0.00025
0.01157	3 grams NaCl	A	0.01151	-0.00006
0.00863	3 grams NaCl	A	0.00854	-0.00009
0.19917	...	B	0.19924	+0.00007
0.10136	...	B	0.10109	-0.00027
0.06769	...	B	0.06774	+0.00005
0.1870	3 grams NaCl	B	0.1870	±0.0000
0.08554	3 grams NaCl	B	0.08581	+0.00027
0.06378	3 grams NaCl	B	0.06406	+0.00028

^a Weight burets employed in final titration.

^b Approximately 0.001 *N* thiosulfate, freshly prepared from 0.1 *N* solution, used in titration.

^c Dilute iodide solution had remained in glass flask overnight before oxidation.

Summary

Iodide and other iodine compounds can be quantitatively oxidized to periodate by ozone in sodium or potassium hydroxide solutions. The periodate formed may be determined by allowing it to react with iodide in excess in a neutral or acid solution, the iodine liberated being titrated with either arsenite or thiosulfate solution.

Amounts of iodide ion varying from several hundredths of a milligram to 0.2 gram can be determined in this manner with considerable accuracy.

Bromides interfere, at least in concentrations greater than 0.6 gram. Chlorides do not interfere.

Complete oxidation requires from 20 to 30 minutes using a gas containing 5 per cent ozone by weight. The sodium hydroxide concentration may vary from 1 per cent to at least 10 per cent.

Literature Cited

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